Organic Chemistry

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Coures Contents

- **Introduction to Organic chemistry:**

  Classification of organic Chemistry

(Alkanes, Alkenes , Alkynes, **Alcohols,** Aldehydes, **Ethers, Ketones, Organic acids and its derivatives**

ALCOHOLS

Alcohols

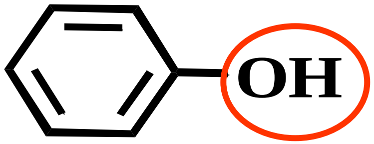
Simple alcohols are named as derivatives of the parent alkane, using the ***<u>suffix -ol</u>***, using the following simple rules:

- Select the longest continuous carbon chain, containing the hydroxyl group, and derive the parent name by replacing the -e ending with -ol.
- Number the carbon chain, beginning at the end nearest to the hydroxyl group.
- Number the substituents and write the name, listing substituents alphabetically.

ALCOHOLS

- **Alcohols**: Organic compounds containing **hydroxyl (-OH)** functional groups.

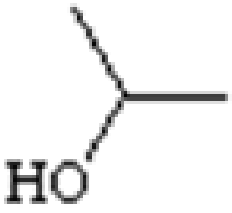
- **Phenols**: Compounds with hydroxyl group bonded directly to an aromatic (benzene) ring.



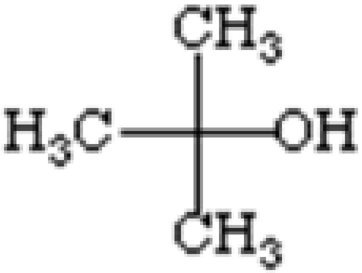
ALCOHOLS ($C_nH_{2n+1}OH$)

Preparation and properties

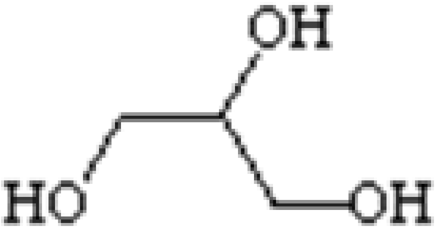
Alcohol Examples



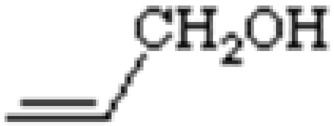
Isopropyl alcohol
(2-propanol)



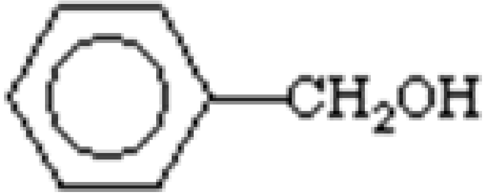
tert-Butyl alcohol
(2-methyl-2-propanol)



Glycerol
(1,2,3-propanetriol)



Allyl alcohol
(2-propen-1-ol)



Benzyl alcohol
(phenylmethanol)

NOMENCLATURE OF ALCOHOLS

IUPAC System

1. **Select the longest continuous chain of carbon atoms containing the hydroxyl group.**

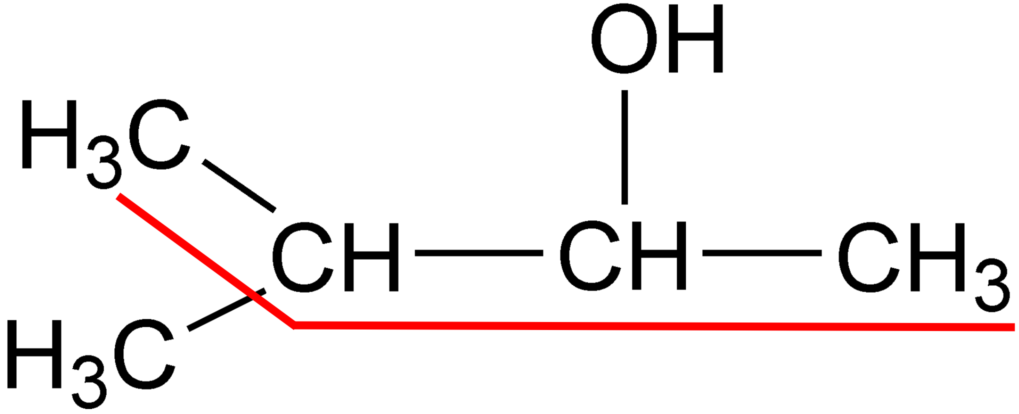
2. **Number the carbon atoms in this chain so that the one bonded to the –OH group has the lowest possible number.**

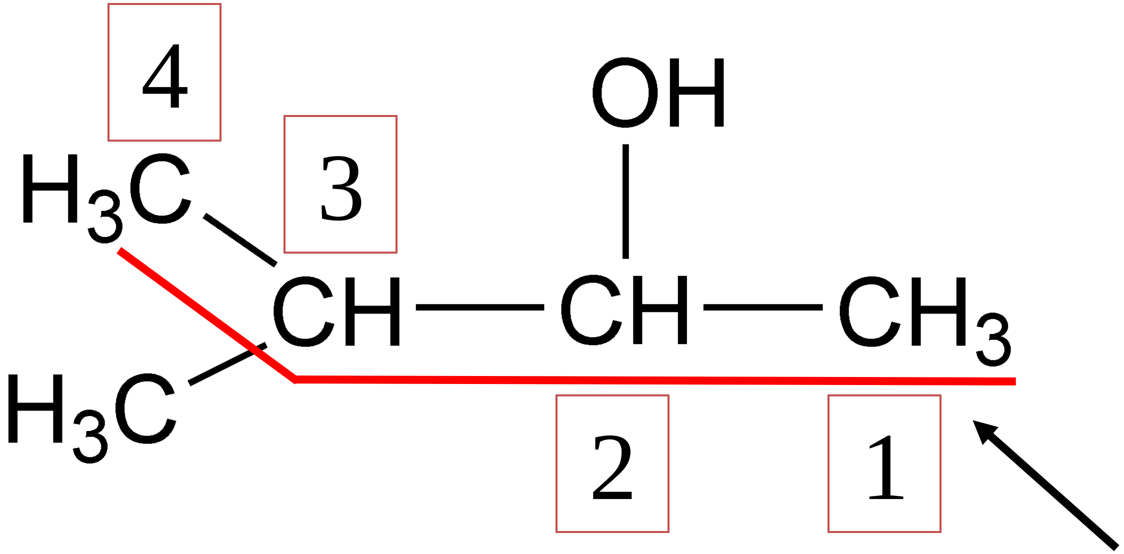
3. **Form the parent alcohol name by replacing the final *–e* of the corresponding alkane name by *–ol* .**

4. **Name each alkyl branch chain (or other group) and designate its position by number.**

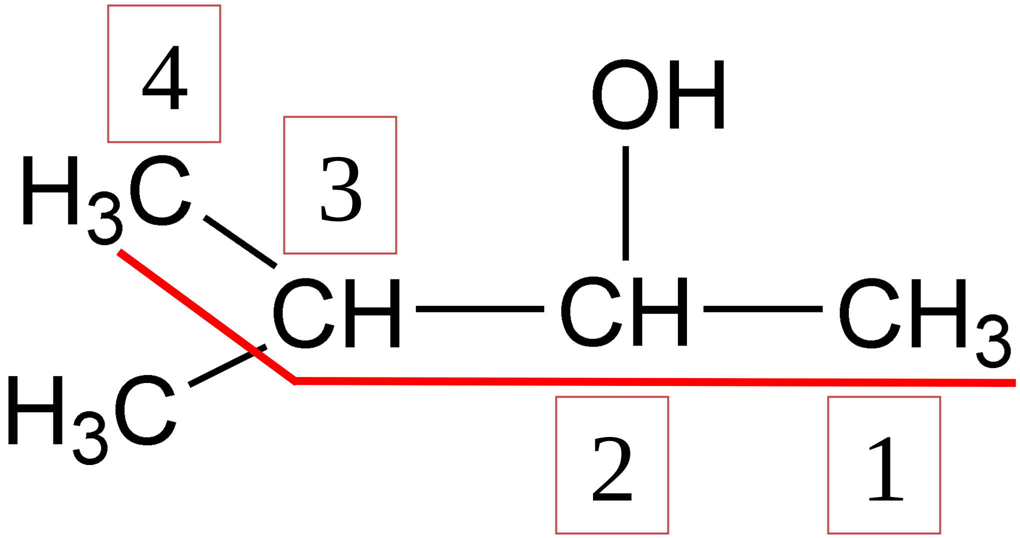
This is the longest continuous chain that contains an hydroxyl group.

Select this chain as the parent compound.





**This end of the chain is closest to the OH.
Begin numbering here.**



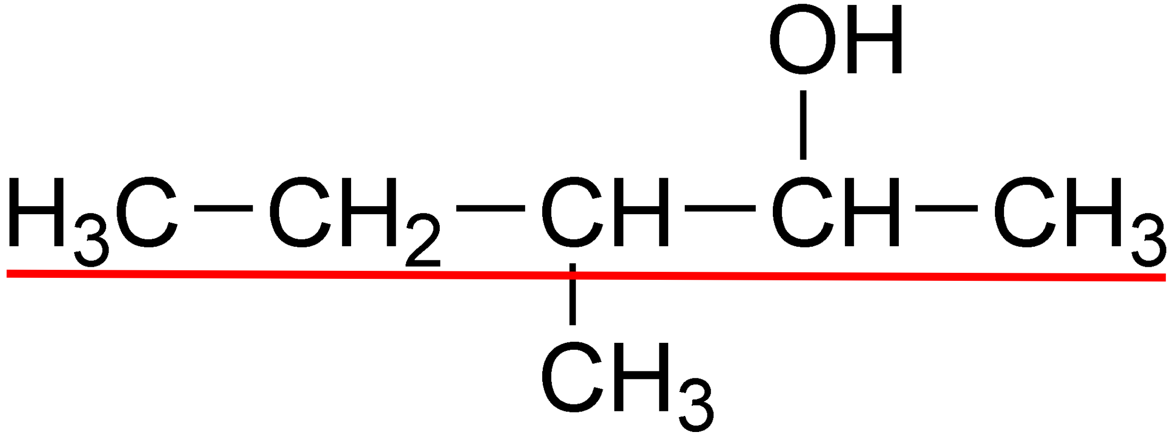
IUPAC name: 3-methyl-2-butanol

New IUPAC name: 3-methylbutan-2-ol

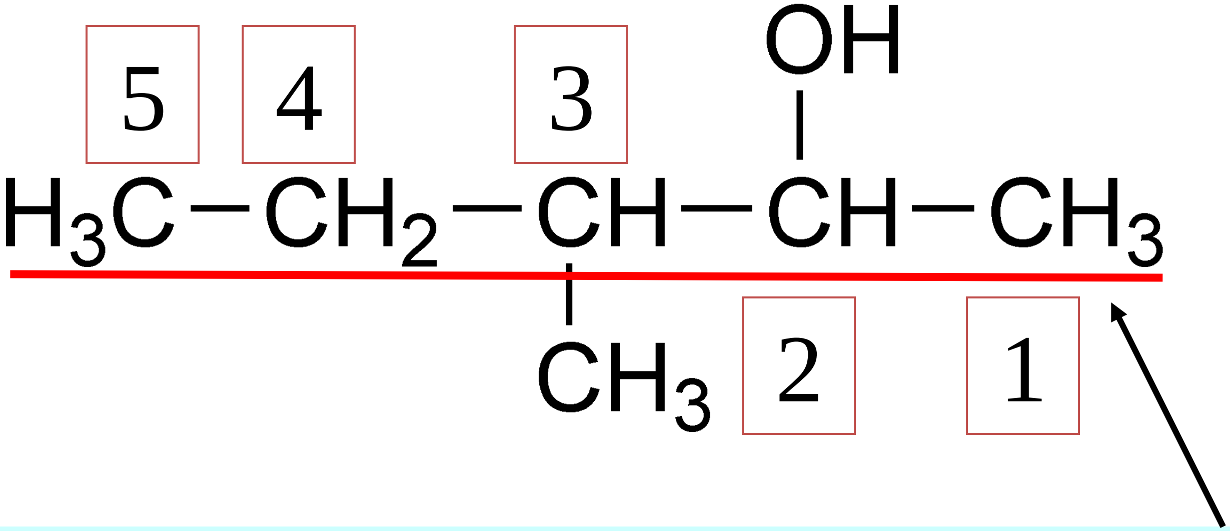
Example:

This is the longest continuous chain that contains an hydroxyl group.

Select this chain as the parent compound.

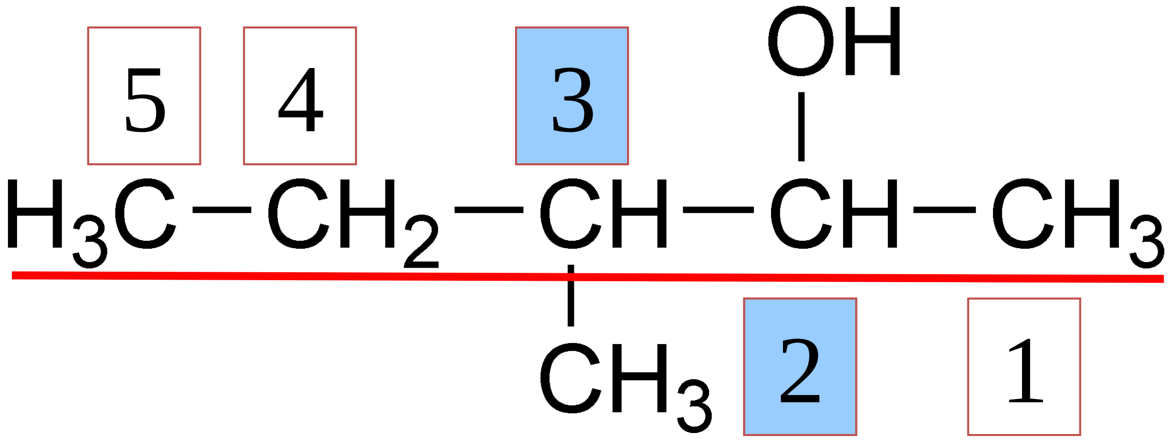


$H_3C-CH_2-\underset{CH_3}{CH}-\overset{OH}{CH}-CH_3$



$H_3C-CH_2-\underset{CH_3}{CH}-\overset{OH}{CH}-CH_3$

This end of the chain is closest to the OH.
Begin numbering here.



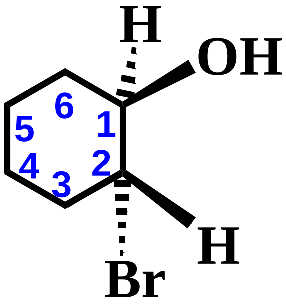
$$H_3C-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_3$$

IUPAC name: 3-methyl-2-pentanol

New IUPAC name: 3-methylpentan-2-ol

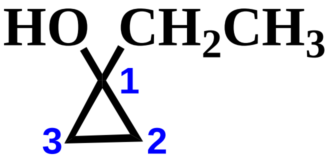
NOMENCLATURE OF CYCLIC ALCOHOLS

- Using the prefix *cyclo*-
- The hydroxyl group is assumed to be on C1.



IUPAC name: *trans*-2-bromocyclohexanol

new IUPAC name: *trans*-2-bromocyclohexan-1-ol



1-ethylcyclopropanol

1-ethylcyclopropan-1-ol

NOMENCLATURE OF ALCOHOLS CONTAINING TWO DIFFERENT FUNCTIONAL GROUPS

- **Alcohol containing double and triple bonds:**

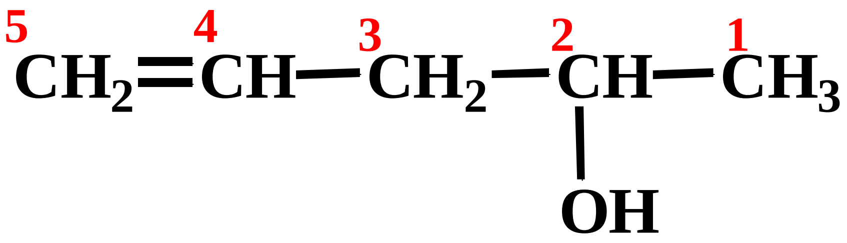
  - use the *–ol* suffix after the alkene or alkyne name.

- **The alcohol functional group takes precedence over double and triple bonds, so the chain is numbered in order to give the lowest possible number to the carbon atom bonded to the hydroxyl group.**

- **The position of the –OH group is given by putting its number before the *–ol* suffix.**

- **Numbers for the multiple bonds were once given early in the name.**

EXAMPLE



$$\overset{5}{\mathrm{C}}\mathrm{H_2}=\overset{4}{\mathrm{C}}\mathrm{H}-\overset{3}{\mathrm{C}}\mathrm{H_2}-\underset{\substack{|\\ \mathrm{OH}}}{\overset{2}{\mathrm{C}}\mathrm{H}}-\overset{1}{\mathrm{C}}\mathrm{H_3}$$

1) Longest carbon chain that contains –OH group
- 5 carbon

2) Position of –OH group
- Carbon-2

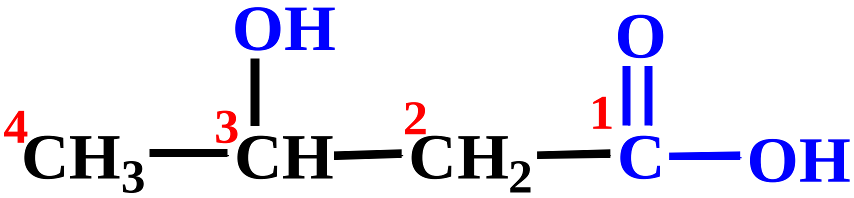
3) Position of C=C
- Carbon-4

COMPLETE NAME = 4-penten-2-ol

- **Some consideration:**

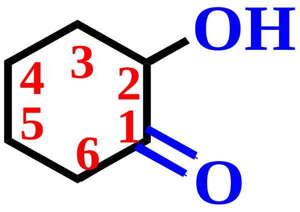
  - OH functional group is named as a hydroxy substituent when it appears on a structure with a higher priority functional group such as acids, esters, aldehydes and ketones.

  - Examples:



$CH_3-CH(OH)-CH_2-C(=O)-OH$

3-hydroxybutanoic acid

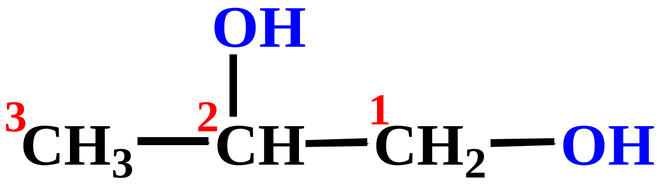


2-hydroxycyclohexanone

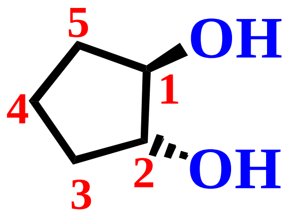
NOMENCLATURE OF DIOLS

- Alcohols with two –OH groups → diols or lycols.

- Naming of diols is like other alcohols except that the suffix diol is used and two numbers are needed to tell where the two hydroxyl groups are located.



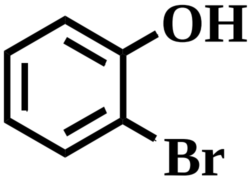
$${}^{3}CH_3-{}^{2}\overset{OH}{\overset{|}{C}H}-{}^{1}CH_2-OH$$

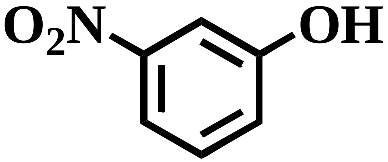


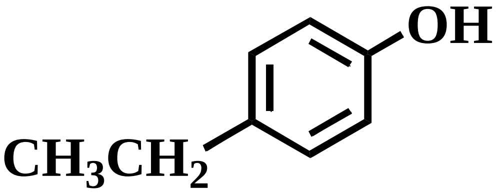
IUPAC name propane-1,2-diol *trans*-cyclopentane-1,2-diol

NOMENCLATURE OF PHENOLS

- The terms *ortho* (1,2-disubstituted), *meta* (1,3-disubstituted) and *para* (1,4-disubstituted) are often used in the common names.

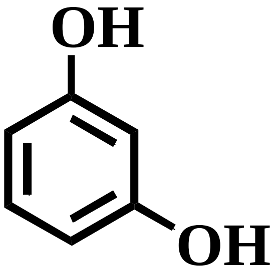




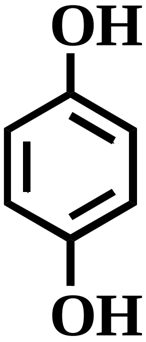


IUPAC name:	2-bromophenol	3-nitrophenol	4-ethylphenol
common name:	*ortho*-bromophenol	*meta*-nitrophenol	*para*-ethylphenol

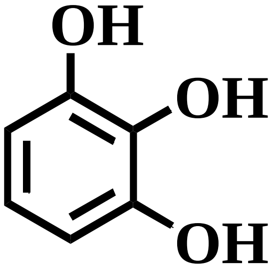
- **Phenols may be monohydric, dihydric or trihydric - (number of hydroxyl groups) in the benzene ring.**



benzene-1,3-diol



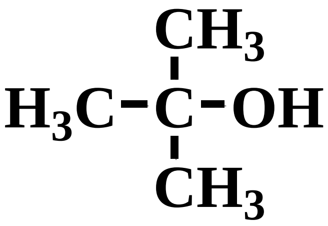
benzene-1,4-diol



benzene-1,2,3-triol

COMMON NAMES

- **Derived from the common name of the *alkyl group* and the word *alcohol*.**
- **For examples:**

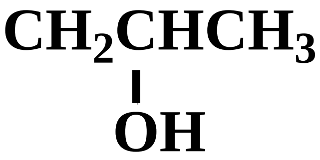


$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H_3C- & C & -OH \\ & | & \\ & CH_3 & \end{array}$$

IUPAC name: 2-methyl-2-propanol
Common name: tert-butyl alcohol

CH_3CH_2OH

IUPAC name: ethanol
Common name: ethyl alcohol



$$\begin{array}{ccc} CH_2 & CH & CH_3 \\ & | & \\ & OH & \end{array}$$

IUPAC name: 2-propanol
Common name: isopropyl alcohol

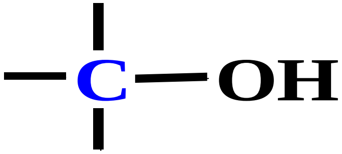
CH_3OH

IUPAC name: methanol
Common name:methyl alcohol

CLASSIFICATION OF ALCOHOLS

CLASSIFICATION

- According to the type of carbinol carbon atom (C bonded to the –OH group).



Classes:

i) **Primary alcohol**

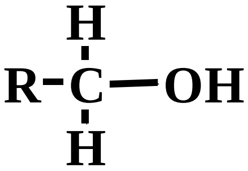
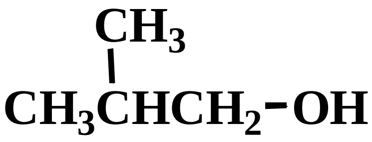
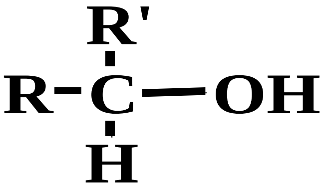
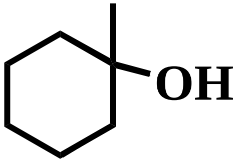
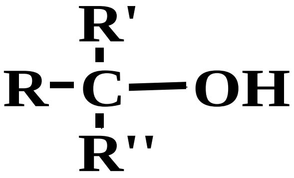
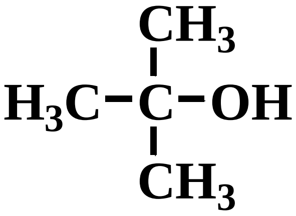
- -OH group attached to a primary carbon atom
- one alkyl group attached

ii) **Secondary alcohol**

- -OH group attached to a secondary carbon atom
- two alkyl group attached

iii) **Tertiary alcohol**

- -OH group attached to a tertiary carbon atom
- three alkyl group attached

TYPE	STRUCTURE	EXAMPLES
Primary (1°) (i	 $R-\overset{H}{\underset{H}{C}}-OH$	CH_3CH_2-OH ethanol  $CH_3\overset{CH_3}{C}HCH_2-OH$ 2-methyl-1-propanol
Secondary (2°)	 $R-\overset{R'}{\underset{H}{C}}-OH$	 $H_3C-\overset{OH}{C}H-CH_2CH_3$ 2-butanol  cyclohexanol
Tertiary (3°) (i	 $R-\overset{R'}{\underset{R''}{C}}-OH$	 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$ 2-methyl-2-propanol

Polyhydroxy Alcohols

1- Alcohols that contain more than one OH group - polyhydroxy alcohols.

2- Monohydroxy: one OH group.

3- Dihydroxy: two OH groups.

4- Trihydroxy: three OH groups.

PHYSICAL PROPERTIES OF ALCOHOLS

PHYSICAL PROPERTIES

- ***PHYSICAL STATES OF ALCOHOLS***

- aliphatic alcohols and lower aromatic alcohols ⟶ liquids at room temperature.

- highly branched alcohols and alcohols with twelve or more carbon atoms ⟶ solids.

- ***BOILING POINTS***

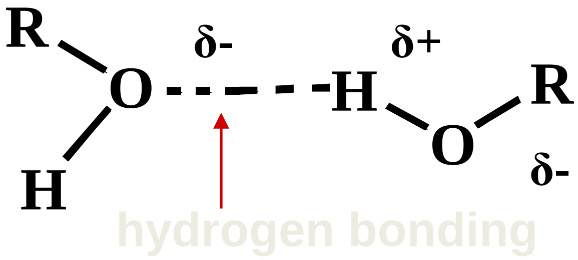
i) Boiling points of alcohols are higher > alkanes and chloroalkanes of similar relative molecular mass.

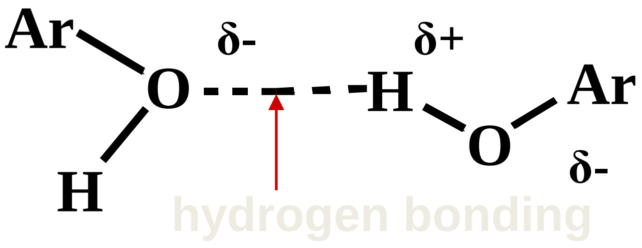
- For example:

	C_2H_5OH	$CH_3CH_2CH_3$	CH_3Cl
Relative molecular mass:	46	44	50.5
Boiling point:	78°C	-42°C	-24°C

- *Reason*:

*** intermolecular hydrogen bonds**





- ***SOLUBILITY OF ALCOHOLS IN WATER***

i) Alcohols with short carbon chains (i.e. methanol, ethanol) -dissolve in water.

- dissolve in water (hydrogen bonds are formed).

ii) Solubility decreases sharply with the increasing length of the carbon chain.

iii) Higher alcohols are insoluble in water.

- alcohol contains a polar end (-OH group) called '*hydrophilic*' and a non-polar end (the alkyl group) called '*hydrophobic*'.

iii) Polyhydroxy alcohols are more soluble than monohydroxy → form more hydrogen bonds with water molecule.

iv) Branched hydrocarbon increases the solubility of alcohol in water → branched hydrocarbon cause the hydrophobic region becomes compact.

ACIDITY OF ALCOHOLS AND PHENOLS

- **Alcohol ⟶ weakly acidic.**
- **In aqueous solution, alcohol will donated its proton to water molecule to give an alkoxide ion (R-O$^-$).**

$$K_a = \sim 10^{-16} \text{ to } 10^{-18} \quad \rightleftharpoons \quad \text{R-O}^- + \text{H}_3\text{O}^+ \qquad \text{R-OH} + \text{H}_2\text{O}$$

alkoxide ion

Example

$$\text{CH}_3\text{CH}_2\text{-O}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{CH}_3\text{CH}_2\text{-OH} + \text{H}_2\text{O}$$

The acid-dissociation constant, *K*a, of an alcohol is defined by the equilibrium

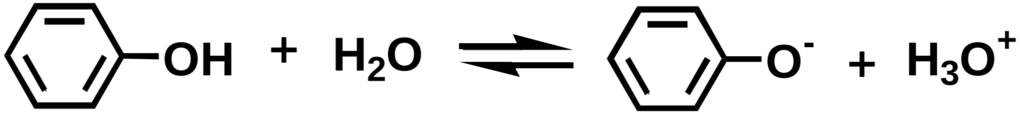
ACIDITY OF PHENOLS

- **Phenol is a stronger acid than alcohols and water.**

$$R\text{-}O^- + H_3O^+ \rightleftarrows R\text{-}OH + H_2O$$

alcohol

alkoxide ion



$K_a = 1.2 \times 10^{-10}$

phenol

phenoxide ion

$$HO^- + H_3O^+ \rightleftarrows H_2O + H_2O$$

hydroxide ion

- **Phenol is more acidic than alcohols by considering the *resonance effect*.**

  i) The alkoxide ion (RO^-)

  - the negative charge is confined to the oxygen and is not spread over the alkyl group.

  - this makes the RO^- ion less stable and more susceptible to attack by positive ions such as H^+ ions.

IMPORTANT OF ALCOHOL

- **Ethanol - solvent for varnishes, perfumes and flavorings, medium for chemical reactions and in recrystallization. Also is an important raw material for synthesis.**

- **Medically, ethanol is classified as a *hypnotic* (sleep producer), it is less toxic than other alcohol.**

- **PREPARATION OF ALCOHOLS**
- **Ethanol is prepared both by hydration of ethylene and by fermentation of sugars. It is the alcohol of alcoholic beverages.**

1) $CH_2{=}CH_2 + H_2O \xrightarrow{\text{acid}} CH_3CH_2OH$

$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2CH_3CH_2OH + 2CO_2$

PREPARATION OF ALCOHOLS

- **Grignard synthesis**
- **Hydrolysis of alkyl halides**

GRIGNARD SYNTHESIS

- **The grignard reagent (RMgX) is prepared by the reaction of metallic magnesium with the appropriate organic halide. This reaction is always carried out in an ether solvent, which is needed to solvate and stabilize the Grignard reagent as it forms.**

$$\text{R-X} + \text{Mg} \xrightarrow{CH_3CH_2OCH_2CH_3} \text{R-Mg-X}$$

(X = Cl, Br or I)

organomagnesium halide

(Grignard reagent)

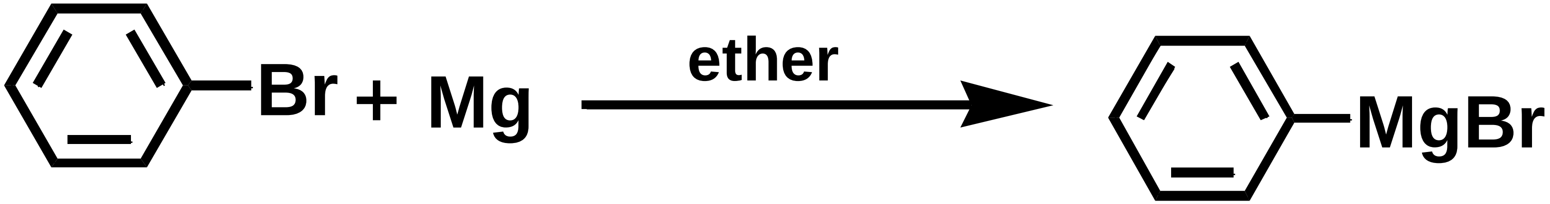
Grignard reagents may be made from primary, secondary, and tertiary alkyl halides, as well as from vinyl and aryl halides.

Alkyl iodides are the most reactive halides, followed by bromides and chloride .

EXAMPLES

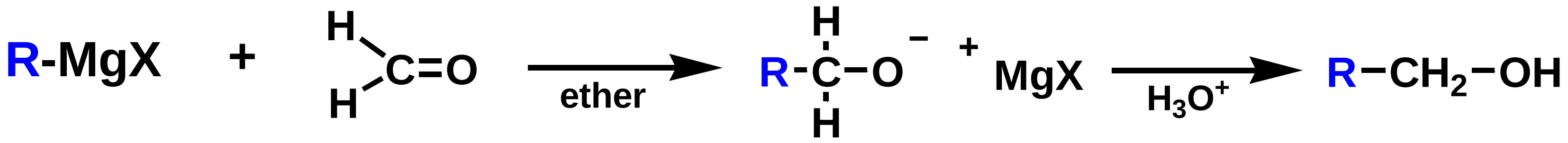
$$CH_3I \quad + \quad Mg \xrightarrow{\text{ether}} CH_3MgI$$

$$CH_3CH_2Br \quad + \quad Mg \xrightarrow{\text{ether}} CH_3CH_2MgBr$$



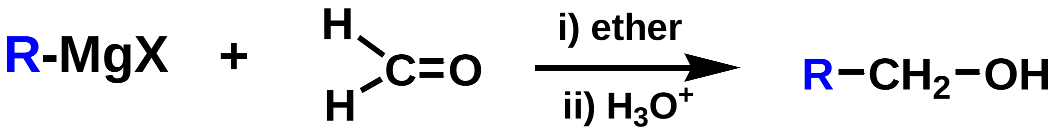
Grignard reactions of carbonyl compounds

- **Formaldehyde ($H_2C=O$) reacts with Grignard reagents giving primary alcohol.**



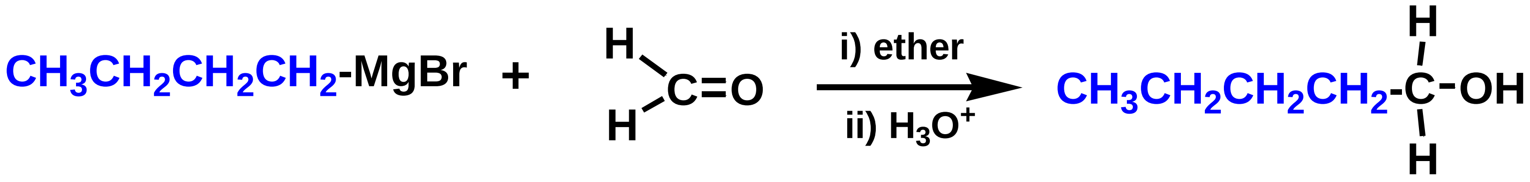
$$R\text{-}MgX + H_2C{=}O \xrightarrow{\text{ether}} R\text{-}CH_2\text{-}O^{-}\ {}^{+}MgX \xrightarrow{H_3O^+} R{-}CH_2{-}OH$$

or



$$R\text{-}MgX + H_2C{=}O \xrightarrow[\text{ii) } H_3O^+]{\text{i) ether}} R{-}CH_2{-}OH$$

Example:

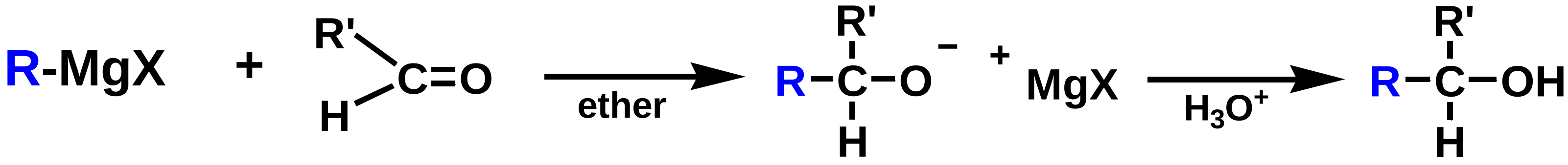


$$CH_3CH_2CH_2CH_2\text{-}MgBr + H_2C{=}O \xrightarrow[\text{ii) } H_3O^+]{\text{i) ether}} CH_3CH_2CH_2CH_2\text{-}CH_2\text{-}OH$$

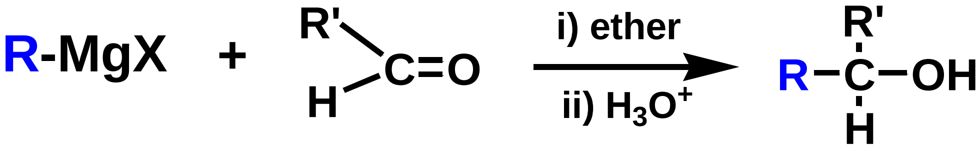
butylmagnesium bromide

1-pentanol (92%)

Aldehydes reacts with Grignard reagents giving secondary alcohols.



or



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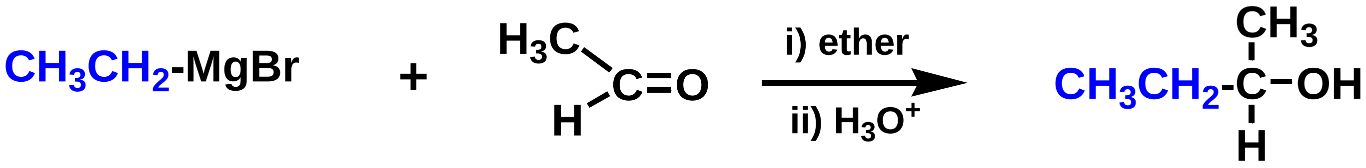
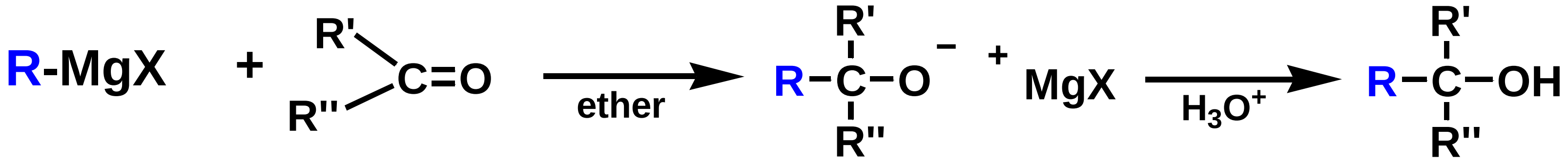


Ketones reacts with Grignard reagents giving tertiary alcohols.



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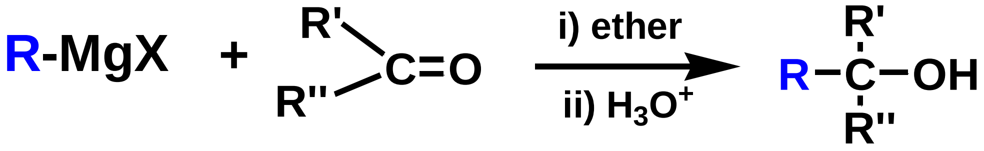
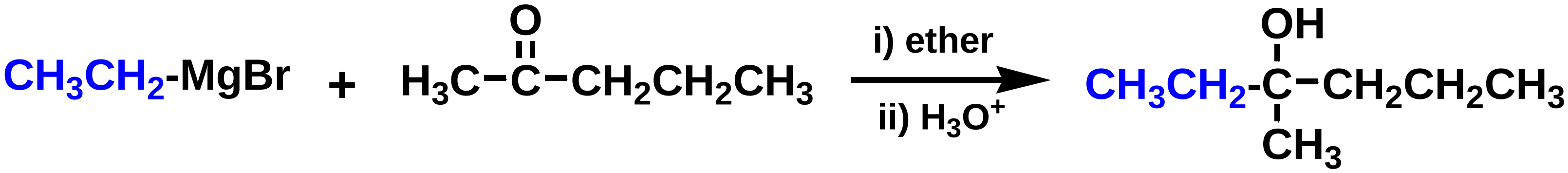


Example:



$$CH_3CH_2\text{-}MgBr + H_3C-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3 \xrightarrow[\text{ii) } H_3O^+]{\text{i) ether}} CH_3CH_2\text{-}\overset{OH}{\underset{CH_3}{C}}-CH_2CH_2CH_3$$

HYDROLYSIS OF ALKYL HALIDES

- **Hydrolysis of alkyl halides is severely limited as a method of synthesizing alcohol, since alcohol are usually more available than the corresponding halides;indeed, the best general preparation of halides is from alcohols.**

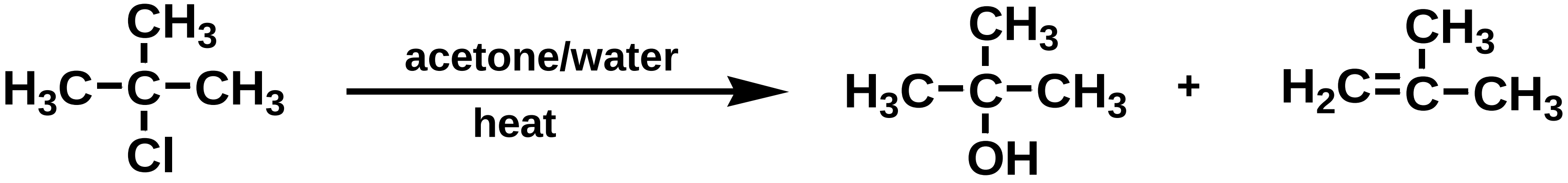
- **For those halides that can undergo elimination, the formation of alkene must always be considered a possible side reaction.**

- **Example:**

1) Second-order substitution: primary (and some secondary halides)

$$(CH_3)_2CHCH_2CH_2\text{-Br} \xrightarrow[H_2O]{KOH} (CH_3)_2CHCH_2CH_2\text{-OH}$$

2) First-order substitution: tertiary (and some secondary) halides



$$H_3C-\overset{CH_3}{\underset{Cl}{C}}-CH_3 \xrightarrow[\text{heat}]{\text{acetone/water}} H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3 \quad + \quad H_2C{=}\overset{CH_3}{C}-CH_3$$

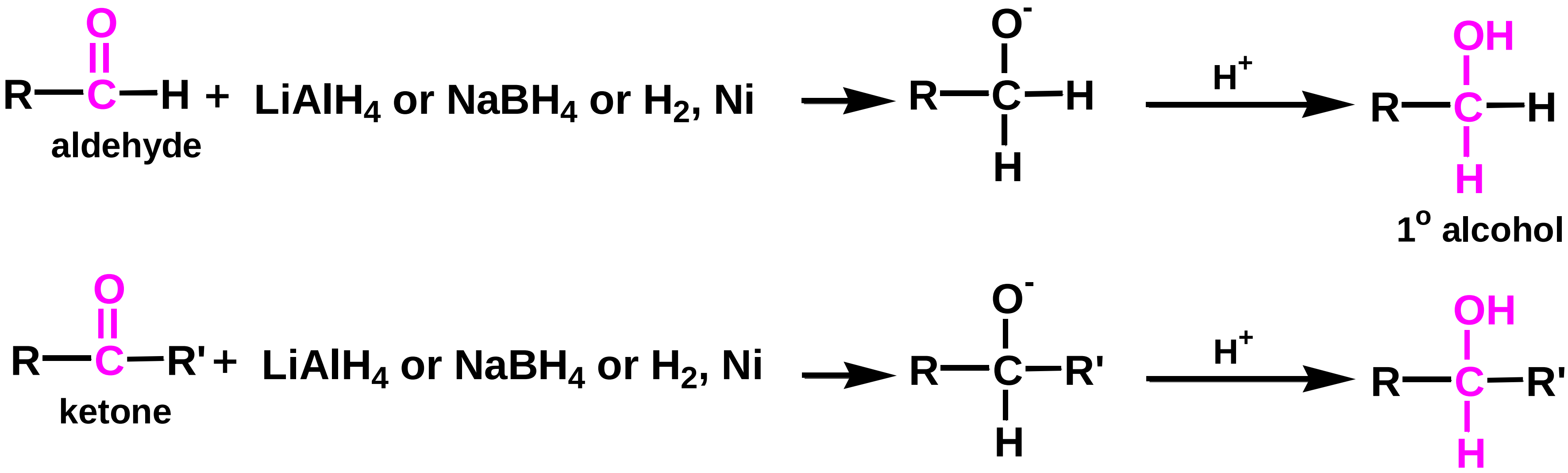
REDUCTION OF ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

- **Aldehydes and ketones can be reduced to alcohols using:**

  a) lithium aluminium hydride ($LiAlH_4$)

  b) sodium borohydride ($NaBH_4$)

  c) catalytic hydrogenation

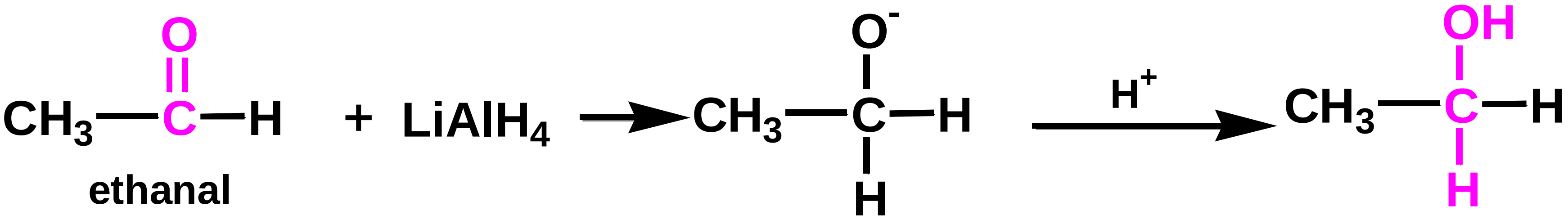


$$R-\overset{O}{\overset{\|}{C}}-H + LiAlH_4 \text{ or } NaBH_4 \text{ or } H_2\text{, Ni} \longrightarrow R-\underset{H}{\overset{O^-}{C}}-H \xrightarrow{H^+} R-\underset{H}{\overset{OH}{C}}-H$$

$$R-\overset{O}{\overset{\|}{C}}-R' + LiAlH_4 \text{ or } NaBH_4 \text{ or } H_2\text{, Ni} \longrightarrow R-\underset{H}{\overset{O^-}{C}}-R' \xrightarrow{H^+} R-\underset{H}{\overset{OH}{C}}-R'$$

H^+ = diluted acid such as H_2SO_4

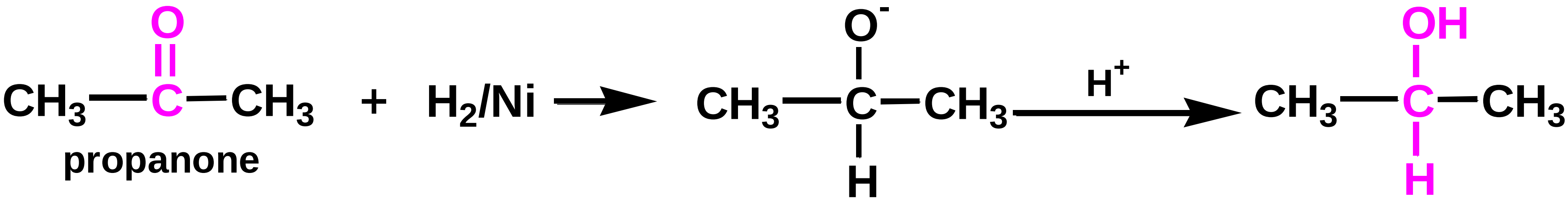
Examples:



$$CH_3-\overset{\overset{\Large O}{||}}{C}-H + LiAlH_4 \longrightarrow CH_3-\overset{O^-}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H \xrightarrow{H^+} CH_3-\overset{OH}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$$

ethanal

ethanol

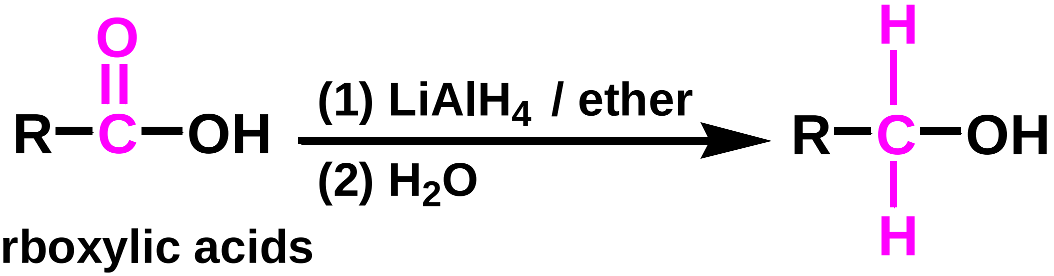


$$CH_3-\overset{\overset{\Large O}{||}}{C}-CH_3 + H_2/Ni \longrightarrow CH_3-\overset{O^-}{\underset{H}{\overset{|}{\underset{|}{C}}}}-CH_3 \xrightarrow{H^+} CH_3-\overset{OH}{\underset{H}{\overset{|}{\underset{|}{C}}}}-CH_3$$

propanone

2-propanol

- **Carboxylic acids $\xrightarrow{\text{reduced}}$ primary alcohols**
- **Reducing agents: $LiAlH_4$ in dry ether**

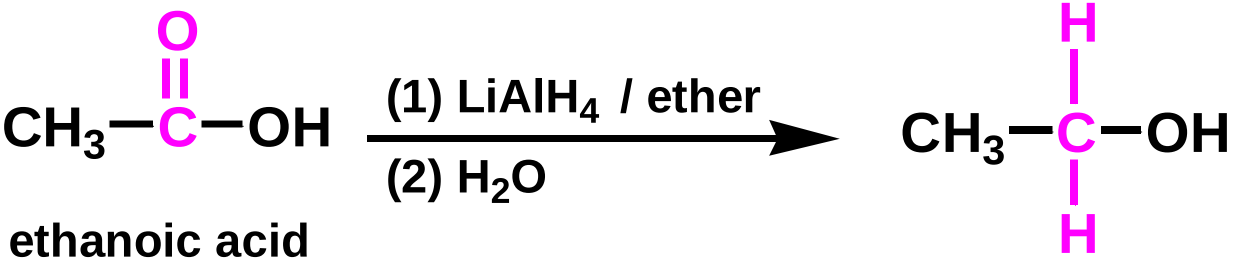


$$R-\overset{\overset{\large O}{\|}}{C}-OH \xrightarrow[\text{(2) } H_2O]{\text{(1) } LiAlH_4 \text{ / ether}} R-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-OH$$

carboxylic acids

primary alcohols

examples:



$$CH_3-\overset{\overset{\large O}{\|}}{C}-OH \xrightarrow[\text{(2) } H_2O]{\text{(1) } LiAlH_4 \text{ / ether}} CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-OH$$

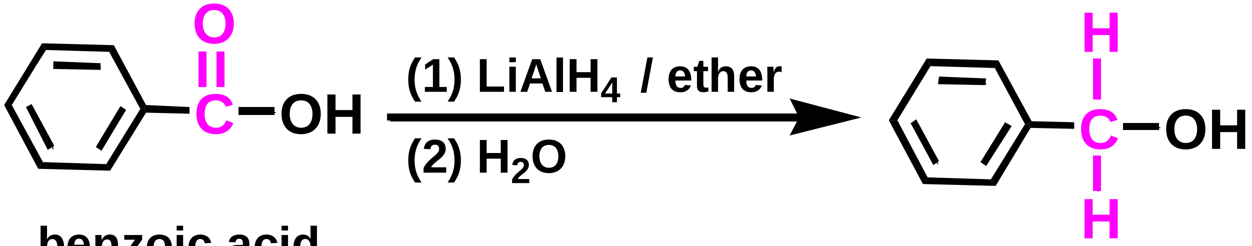
ethanoic acid

ethanol

Benzoic acid can be reduced to phenylmethanol by using $LiAlH_4$ in ether at low temperatures.

An alkoxide intermediate is formed first.

On adding water, hydrolysis of the intermediate yields the primary alcohols.



benzoic acid

phenylmethanol

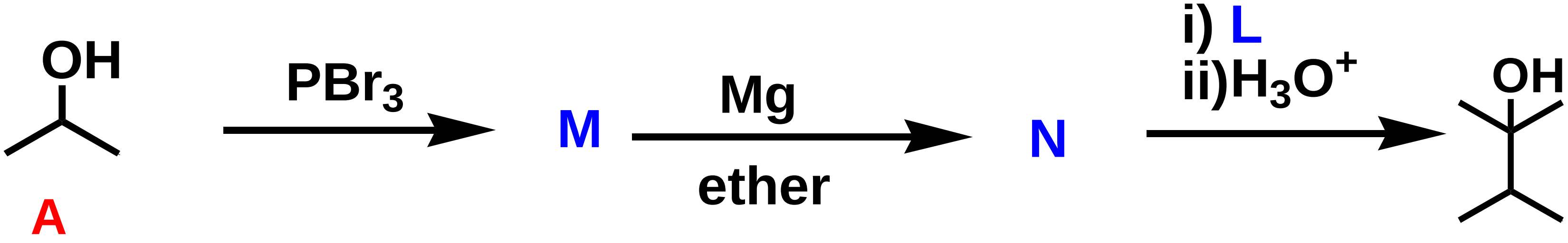
$LiAlH_4$ has no effect on the benzene ring or the double bond.

$-COOH$ is reduced to $–CH_2OH$ but the C=C bonds remains unchanged.

$$CH_3CH_2CH{=}CHCH_2OH \xrightarrow[2)\ H_2O]{1)\ LiAlH_4} CH_3CH_2CH{=}CHCOOH$$

Question:

i) Give the structural formulae of L, M and N

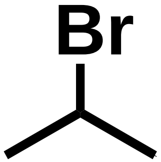


ii) How to prepare alcohol A from the reduction process?

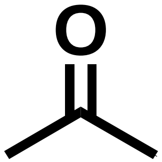
Answers

i)

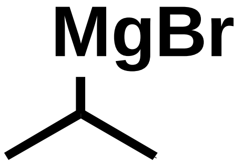
M:



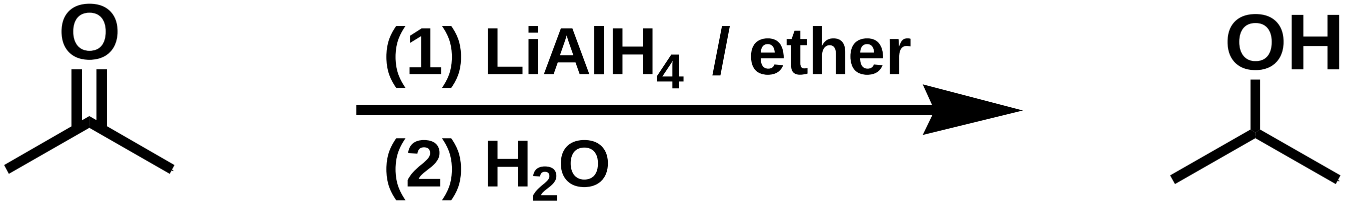
L:



N:



ii)



(1) $LiAlH_4$ / ether

(2) H_2O

REACTIONS OF ALCOHOLS

- **Reaction with sodium**
- **Oxidation**
- **Esterification**
- **Halogenation and haloform reactions**
- **Dehydration**
- **Formation of ether (Williamson ether synthesis)**

Reaction with sodium

- **Alcohols reacts with Na at room temperature to form salts (sodium alkoxides) and hydrogen.**

$$2R\text{-}O\text{-}H + 2Na \rightarrow 2R\text{-}O^{-}\,Na^{+} \quad + \quad H_2$$

For example:

$$CH_3CH_2OH + Na \rightarrow CH_3CH_2O^{-}Na^{+} \;+\; 1/2H_2$$

sodium ethoxide

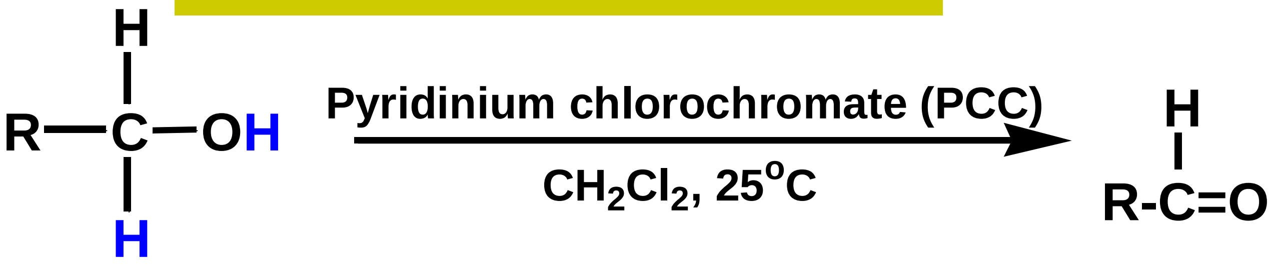
alcohol

Reactivity of alcohols towards the reactions with sodium:

$$CH_3 > 1^\circ > 2^\circ > 3^\circ$$

Oxidation

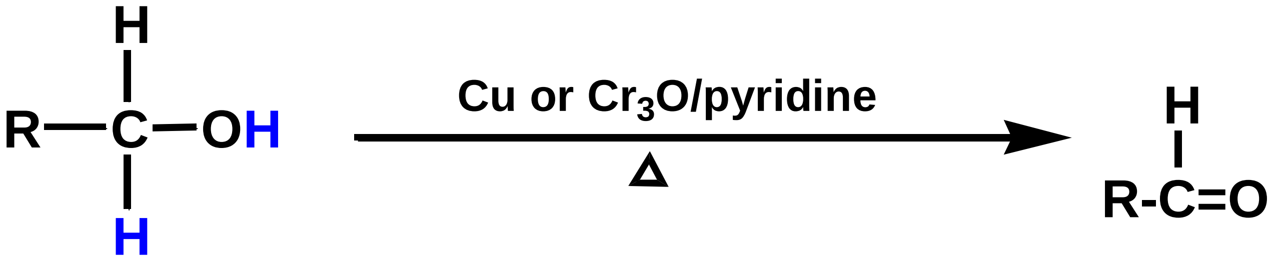
1° alcohol



$$R-\underset{H}{\overset{H}{C}}-OH \xrightarrow[\text{CH}_2\text{Cl}_2\text{, }25^{o}\text{C}]{\text{Pyridinium chlorochromate (PCC)}} R-\overset{H}{C}=O$$

1^{o} alcohol

aldehyde

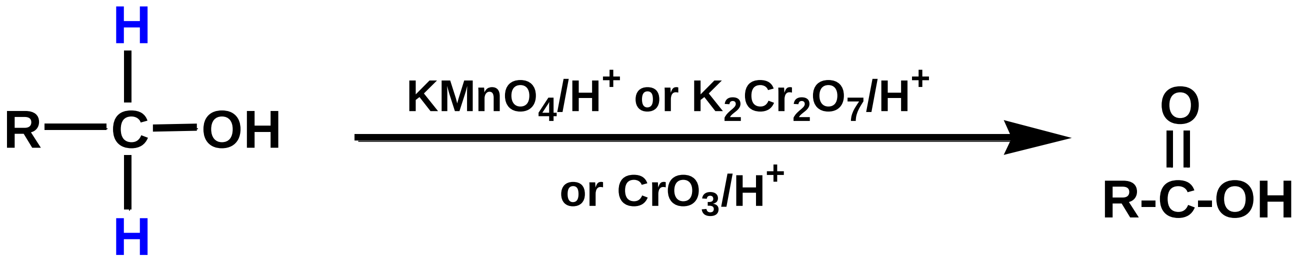


$$R-\underset{H}{\overset{H}{C}}-OH \xrightarrow[\Delta]{\text{Cu or Cr}_3\text{O/pyridine}} R-\overset{H}{C}=O$$

1^{o} alcohol

aldehyde

Cr_3O/pyridine = Collins reagent



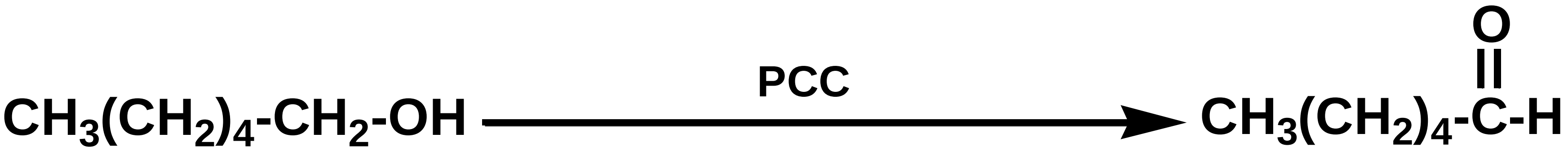
$$R-\underset{H}{\overset{H}{C}}-OH \xrightarrow[\text{or CrO}_3\text{/H}^+]{\text{KMnO}_4\text{/H}^+\text{ or K}_2\text{Cr}_2\text{O}_7\text{/H}^+} R-\overset{O}{\overset{\|}{C}}-OH$$

1^{o} alcohol

carboxylic acid

Examples:

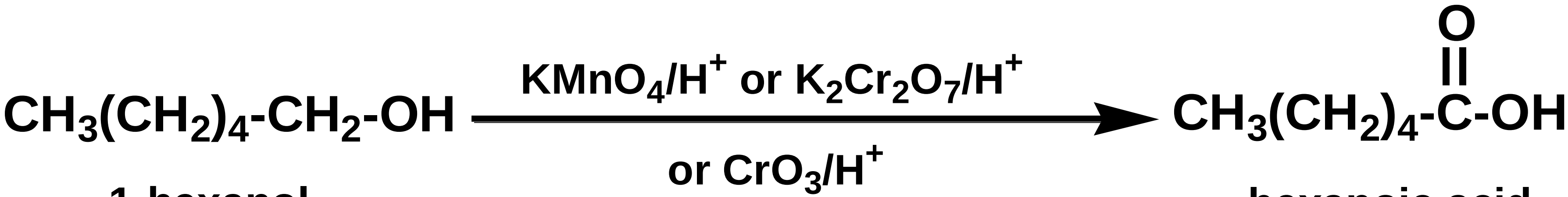
1° alcohol



$$\mathrm{CH_3(CH_2)_4\text{-}CH_2\text{-}OH} \xrightarrow{\mathrm{PCC}} \mathrm{CH_3(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}\text{-}H}$$

1-hexanol

hexanal

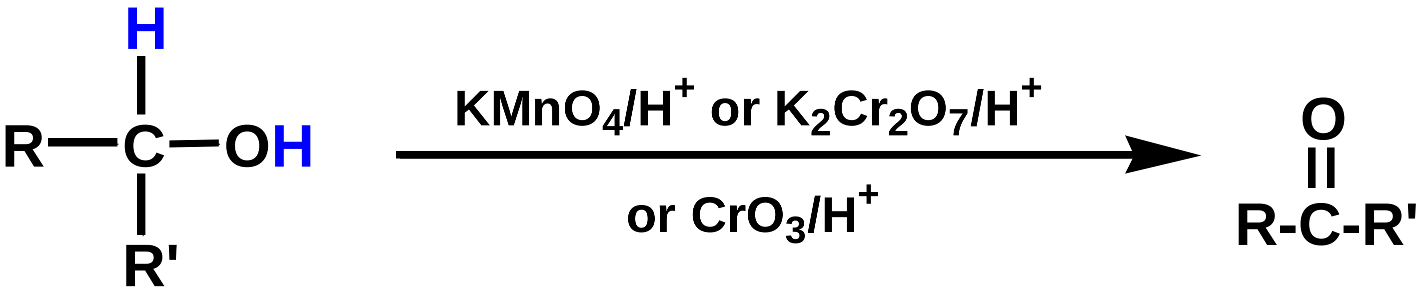


$$\mathrm{CH_3(CH_2)_4\text{-}CH_2\text{-}OH} \xrightarrow[\mathrm{or\ CrO_3/H^+}]{\mathrm{KMnO_4/H^+\ or\ K_2Cr_2O_7/H^+}} \mathrm{CH_3(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH}$$

1-hexanol

hexanoic acid

2° alcohol

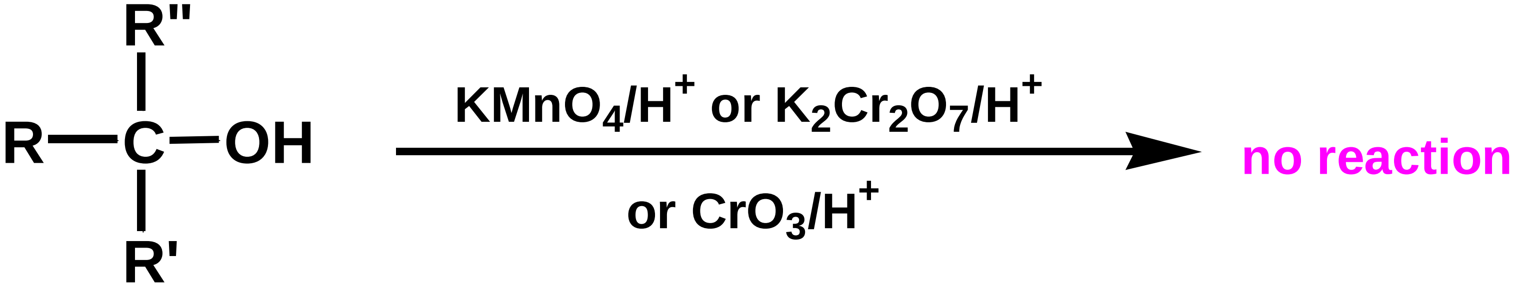


$$R-\overset{\displaystyle H}{\underset{\displaystyle R'}{C}}-OH \xrightarrow[\text{or } CrO_3/H^+]{KMnO_4/H^+ \text{ or } K_2Cr_2O_7/H^+} R-\overset{\displaystyle O}{\overset{\|}{C}}-R'$$

2° alcohol

ketone

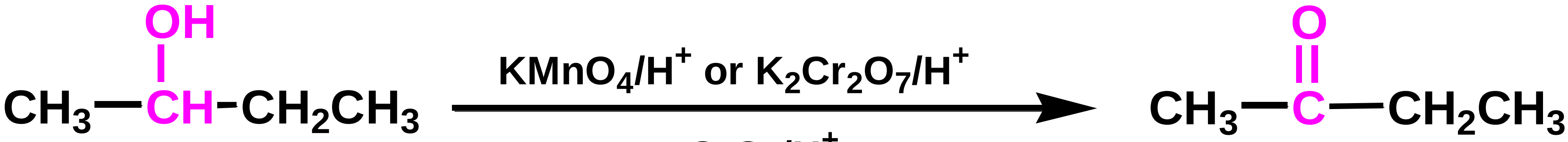
3° alcohol



$$R-\overset{\displaystyle R''}{\underset{\displaystyle R'}{C}}-OH \xrightarrow[\text{or } CrO_3/H^+]{KMnO_4/H^+ \text{ or } K_2Cr_2O_7/H^+} \text{no reaction}$$

3° alcohol

Example:



$$CH_3-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_2CH_3 \xrightarrow[\text{or } CrO_3/H^+]{KMnO_4/H^+ \text{ or } K_2Cr_2O_7/H^+} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2CH_3$$

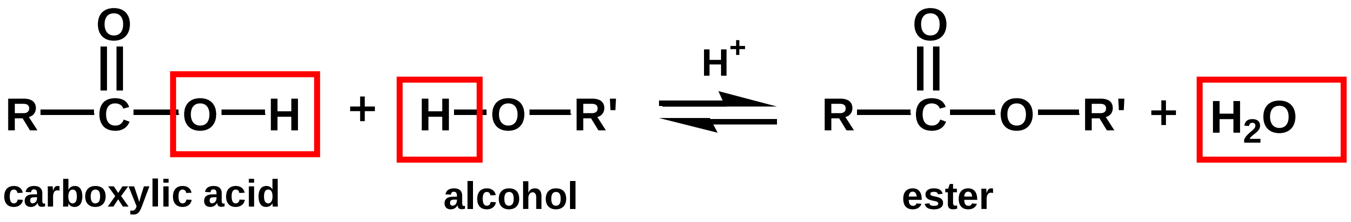
2-butanol

2-butanone

Esterification

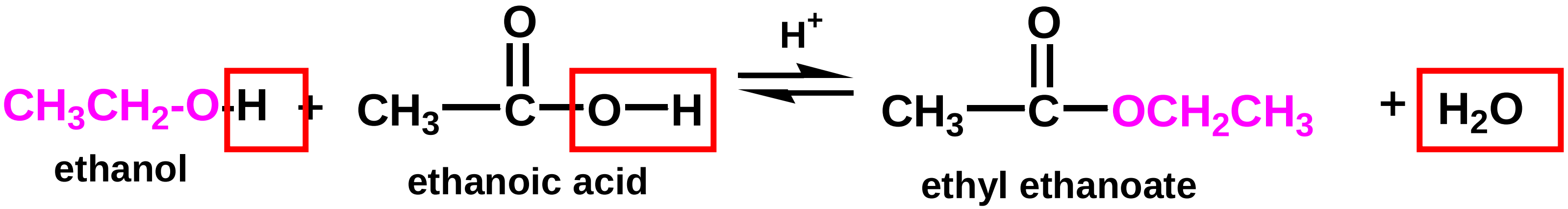
- **Esterification:**

- the reaction between an alcohol and a carboxylic acid to form an ester and H_2O.

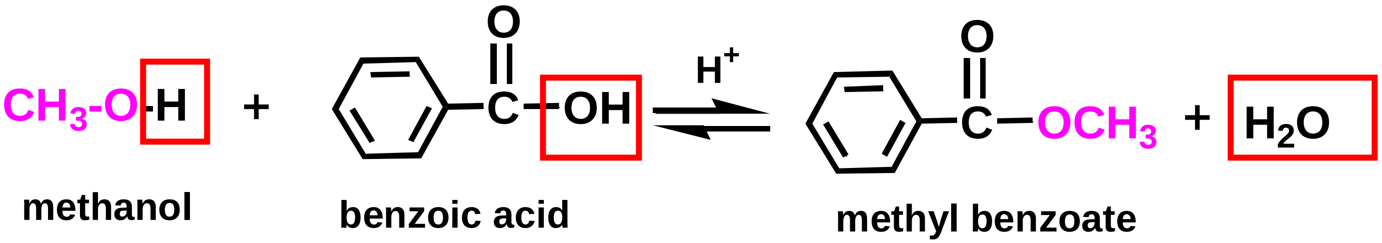


$$R-\overset{O}{\overset{\parallel}{C}}-\boxed{O-H} + \boxed{H}-O-R' \xrightleftharpoons{H^+} R-\overset{O}{\overset{\parallel}{C}}-O-R' + \boxed{H_2O}$$

EXAMPLES

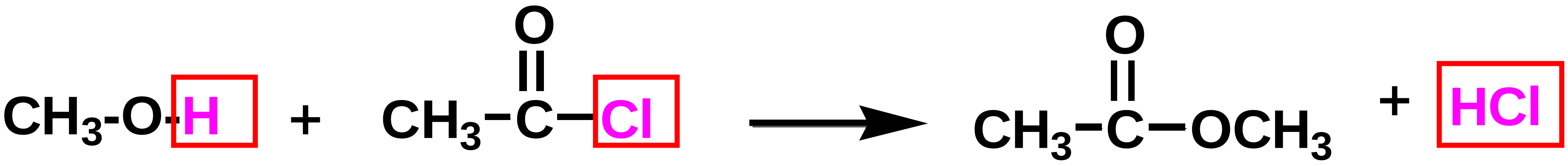


$$CH_3CH_2\text{-}O\boxed{H} + CH_3-\overset{O}{\overset{\parallel}{C}}-\boxed{O-H} \xrightleftharpoons{H^+} CH_3-\overset{O}{\overset{\parallel}{C}}-OCH_2CH_3 + \boxed{H_2O}$$



H^+ = catalyst

Esterification also occurs when alcohols react with derivatives of carboxylic acids such as acid chlorides



$$CH_3\text{-}O\text{-}\boxed{H} + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{Cl} \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 + \boxed{HCl}$$

methanol

ethanoyl chloride

methyl ethanoate

Halogenation and haloform reactions

1) Hydrogen halides (HBr or HCl or HI)

$$R\text{-}OH + H\text{-}X \rightarrow R\text{-}X + H_2O$$

Example:

$$C_2H_5\text{-}OH + H\text{-}Br \xrightarrow{H^+} C_2H_5\text{-}Br + H_2O$$

- Reactivity of hydrogen halides decreases in order HI > HBr > HCl
- Reactivity of alcohols with hydrogen halides:

3° > 2° > 1°

2) Phosphorus trihalides, PX_3 or phosphorus pentahalides, PX_5

$$3R\text{-}OH + PX_3 \xrightarrow{\Delta} 3R\text{-}X + H_3PO_3$$

(PX_3 = PCl_3 or PBr_3 or PI_3)

Example:

$(CH_3)_2CHCH_2\text{-}OH + PBr_3 \rightarrow (CH_3)_2CHCH_2\text{-}Br$

isobutyl alcohol **isobutyl bromide**

3) Thionyl chloride ($SOCl_2$)

$$R\text{-}OH + SOCl_2 \rightarrow R\text{-}Cl + SO_2 + HCl$$

Example:

$CH_3(CH_2)_5CH_2\text{-}OH + SOCl_2 \rightarrow CH_3(CH_2)_5CH_2\text{-}Cl + SO_2 + HCl$

1-heptanol **1-chloroheptane**

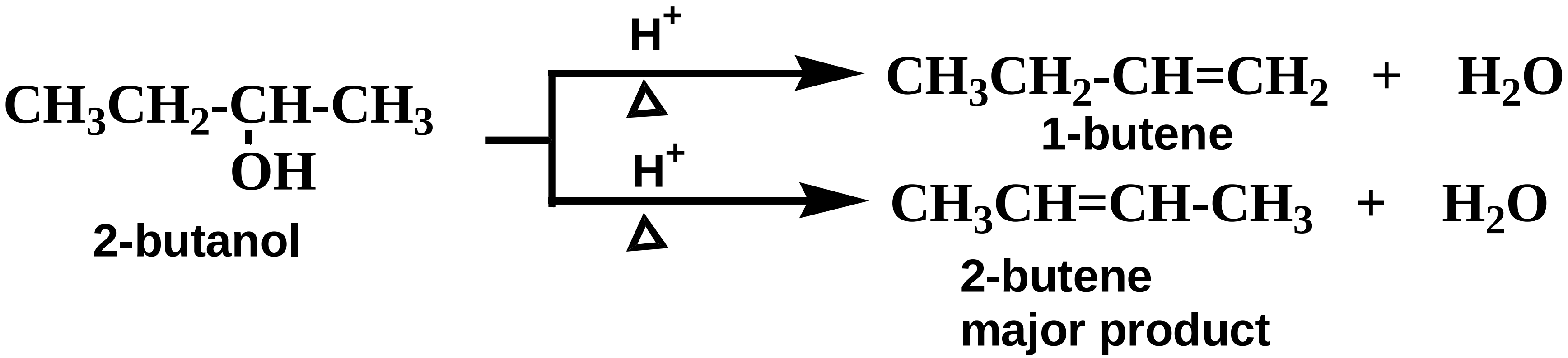
Dehydration

- Dehydration of alcohols will formed alkenes and the products will followed *Saytzeff* rules.

$$\text{R-CH}_2\text{-CH}_2\text{-OH} \xrightarrow[\triangle]{\text{conc. } H_2SO_4} \text{R-CH=CH}_2 + H_2O$$

Saytzeff rule:

- A reaction that produces an alkene would favour the formation of an alkene that has the greatest number of substituents attached to the C=C group.



$$\underset{\text{OH}}{\text{CH}_3\text{CH}_2\text{-}\underset{|}{\text{CH}}\text{-CH}_3}$$

2-butanol

$\xrightarrow[\triangle]{H^+}$ $\text{CH}_3\text{CH}_2\text{-CH=CH}_2 + H_2O$

1-butene

$\xrightarrow[\triangle]{H^+}$ $\text{CH}_3\text{CH=CH-CH}_3 + H_2O$

2-butene

major product

- **Reactivity of alcohols towards dehydration:**

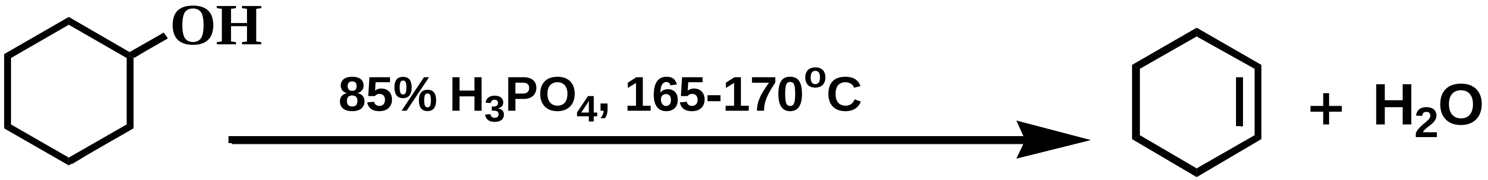
  3° > 2° > 1°

- **Reagents for dehydration:**

  i) Concentrated H_2SO_4

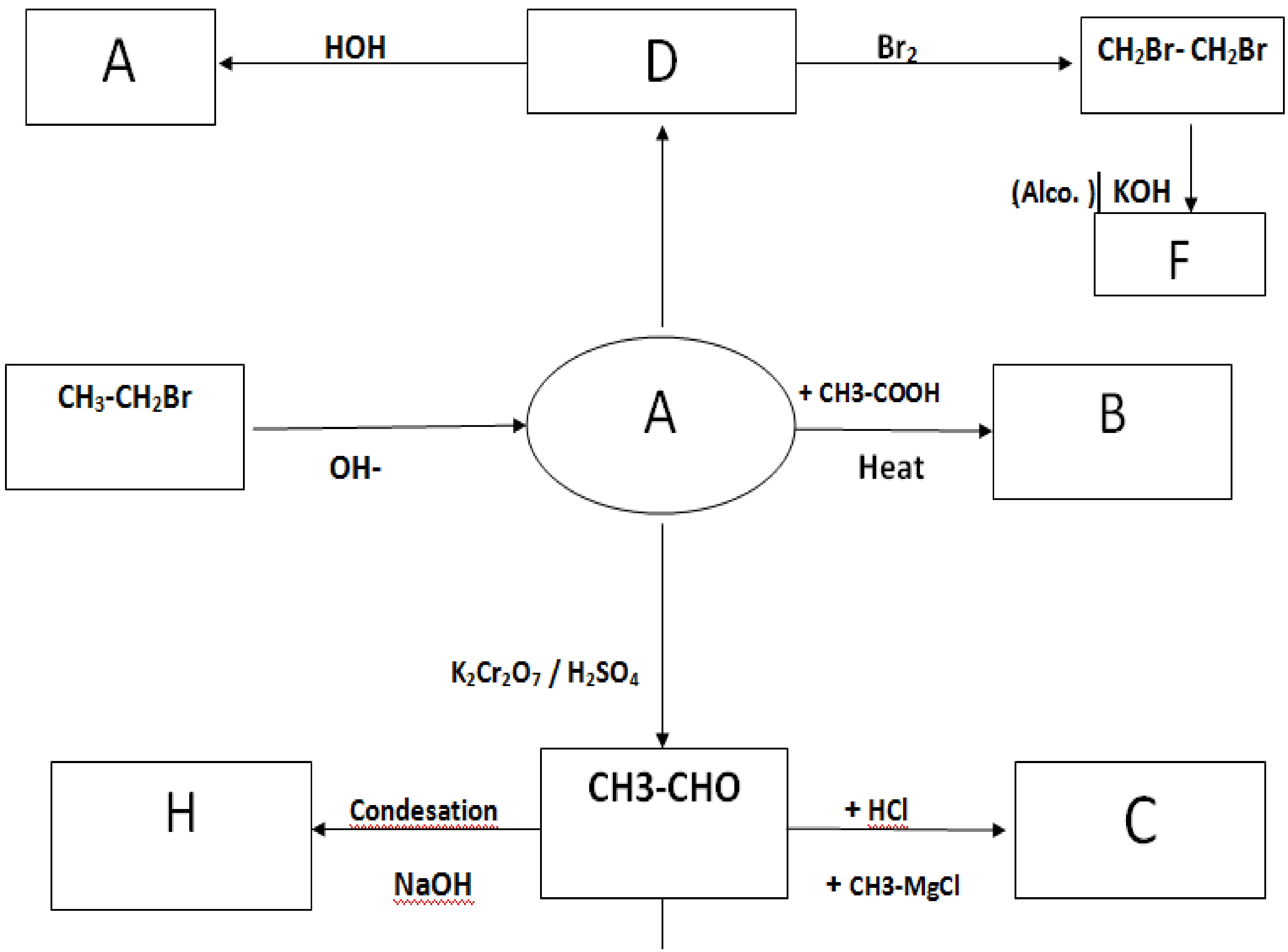
$$CH_3\text{-}CH_2\text{-}OH \xrightarrow[\triangle]{\text{conc. } H_2SO_4} CH_2{=}CH_2 + H_2O$$

ii) With phosphoric (v) acid



iii) Vapour phase dehydration of alcohols

$$CH_2{=}CH_2 + H_2O \xrightarrow[\text{heat}]{Al_2O_3} CH_3CH_2OH$$


A
HOH
D
Br₂
CH₂Br- CH₂Br
(Alco.) KOH
F
CH₃-CH₂Br
OH-
A
+ CH3-COOH
Heat
B
K₂Cr₂O₇ / H₂SO₄
H
Condesation
NaOH
CH3-CHO
+ HCl
+ CH3-MgCl
C